E1. Kinetics of the Formation of Iron Nanoparticles in the Gas Phase

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The magnetic and electronic properties of iron open a wide field of practical applications for iron particles. Various techniques for the synthesis of nano powders are known [1]. Gas-phase synthesis allows the production of very small particles with high purity and uniform composition. For a better understanding and description of the formation processes kinetic data are necessary. The synthesis of iron particles via the gas-phase route is strongly controlled by the decomposition of the precursor, usually iron pentacarbonyl (IPC), the kinetics of single iron cluster formation and the further growth of the clusters and particles. The rate coefficients of the iron pentacarbonyl decomposition and of the formation of first clusters were determined in a shock-tube. Atomic Resonance Absorption Spectrometry (ARAS) for the measurement of the Fe-atom concentration and Molecular Resonance Absorption Spectrometry (MRAS) for the measurement of the CO concentration were used. The further growth of the clusters was observed by Time-Resolved Laser-Induced Incandescence (TR-LII) which allows an in-situ measurement of the particle size.

The iron pentacarbonyl decomposition, which was measured in the temperature range of 540 to 730 K with IPC concentrations of 5 and 10 ppm, shows a uniform decrease of the CO signals. Therefore, no individual decomposition reactions could be determined. Together with the Fe atom concentration profiles an Arrhenius expression

$$k_{\text{global}} = 1.93 * 10^9 \exp(-8700 \text{ K} / T) \text{ s}^{-1}$$

was found for the reaction

$$Fe(CO)_5 \rightarrow Fe + 5 CO.$$
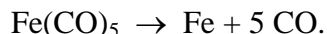
The formation of first clusters was studied in the temperature range of 670 to 1150 K with IPC concentrations of 30 and 100 ppm. Because of the higher concentrations a less sensitive Fe-absorption line was chosen. At the upper experimental temperature limit, the experiments showed constant Fe-atom concentration levels after decomposition of the precursor. At lower temperature, a time-dependent decrease of the Fe concentration was observed showing an inverse temperature dependence. A simplified reaction mechanism consisting of a two step decomposition of the precursor and various iron consumption reactions was proposed for the simulation of the signals. The major initial reactions for the understanding of the condensation process were found to be the formation and decomposition of Fe_2:

$$Fe + Fe + M \rightarrow Fe_2$$
$$Fe_2 + M \rightarrow Fe + Fe + M$$
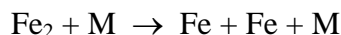
The rate coefficients of both reactions were determined experimentally to be:

$k_{for} = 10^{19}$ cm^6 mol^{-2} s^{-1} and

$k_{rev} = 10^{19.63\pm0.4}$ exp(-17800 ± 700 K / T) cm^3 mol^{-1} s^{-1}.

The further growth of the clusters and particles was studied with an IPC concentration of 0.5% by two-color TR-LII at post-shock temperatures of about 920 and 1120 K. The results are summarized in Fig. 1. The growth curve is independent of the temperature. This is confirmed by numerical simulations that use a simple model which is based on chemical reaction, homogeneous nucleation, surface growth, coagulation and coalescence. A detailed description of the measurement method is given by Kock et al. [2].
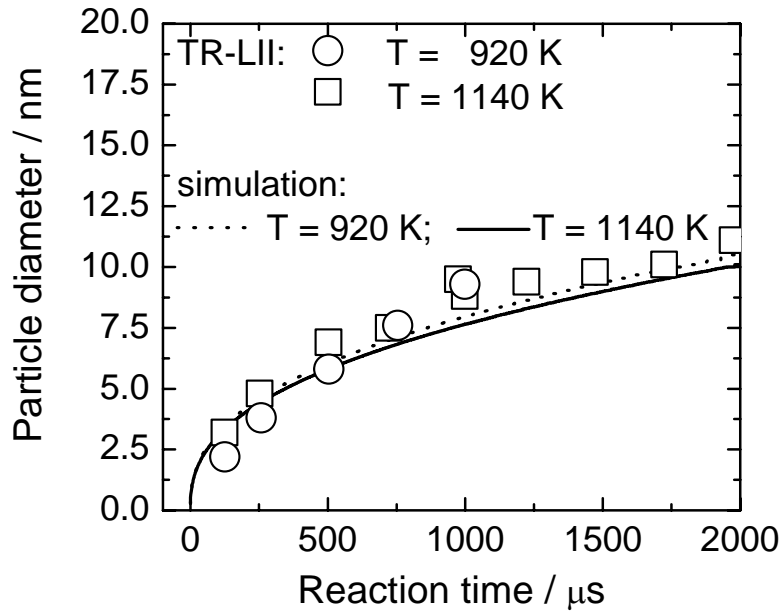

Fig. 1 Experimental and simulated growth curve of iron nanoparticles.

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E2. Complete Thermodynamically Consistent Kinetic Model for Particle Nucleation and Growth: Comparison with the Classical Nucleation Theory

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A complete thermodynamically consistent elementary reaction kinetic model of particle nucleation and growth from supersaturated solutions was developed and evaluated. The model treats all processes recognized in the aerosol science (such as nucleation, condensation, evaporation, agglomeration/coagulation, etc.) as reversible elementary reactions. It includes all possible forward reactions (i.e., of monomers, dimers, trimers, etc.) together with the thermodynamically consistent reverse processes:

$$P_i \quad + \quad P_j \quad \rightleftharpoons \quad P_{i+j} \qquad i, j = 1, 2, 3 \ldots \infty \qquad (1)$$
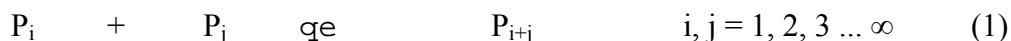
where P_1, P_2, P_3, ..., are the monomers, dimers, trimers, etc. The surface tension approximation for the particle thermodynamics and the simple collision theory for the forward processes (the assumptions accepted in the classical nucleation theory) were used. The model parameters are S_0 – the initial supersaturation and N_{crit} – the initial critical nucleus size. This kinetic model was numerically evaluated over the ranges of S_0 and N_{crit}. The time evolution of the size distribution function was obtained. The results were compared with the predictions of the classical nucleation theory. The validity and the impact of the basic assumptions of the classical nucleation theory (such as the existence of the steady-state regime for clusters smaller than the critical nucleus, constant particle flux) was assessed and the applicability limits of the theory were outlined. The conditions at which the classical nucleation theory is applicable are illustrated in Fig. 1. The region of parameters inside the dashed area is the region where the solutions satisfy the major assumptions of the classical nucleation theory (the criterion was the stability of the flux within 20% over a time interval wider than a factor of 3, $t_{fin} > 3\ t_{ini}$). Outside the dashed area no steady-state and no constant particle flux is established.

The impact of the thermodynamic consistency (treatment of all processes as reversible) compared with previously developed partially reversible kinetic models was assessed. The difference in the particle concentration in these approaches could be as large as 2 - 3 orders of magnitude at some conditions.

Model calculations were performed for nano-particle formation by Rapid Expansion of Supercritical Solutions (RESS) and compared with the experimental observations.
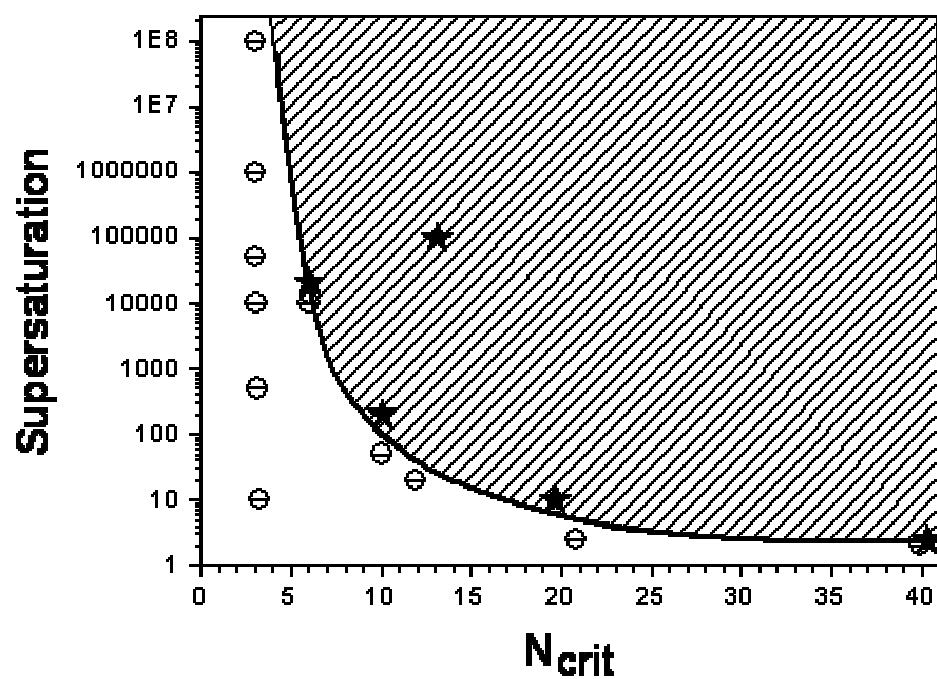
Figure 1. Dashed area – a two-dimensional region of parameters S_0 and N_{crit} where classical theory of nucleation is applicable. In calculations that are labeled by circles the particle flux did not stabilize at any time. Stars – the particle flux satisfied the criteria.

E3. Interactions and Reactions of Water Clusters on Graphite

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The properties, interactions, and reactions of water clusters $(H_2O)_{n=1-5}$ on model systems for a graphite surface shown in **Figure 1** have been studied using pure B3LYP, dispersion-augmented density functional tight binding (DFTB-D), and integrated ONIOM(B3LYP:DFTB-D) methods. Coronene $C_{24}H_{12}$, as well as polycircumcoronenes $C_{96}H_{24}$ and $C_{216}H_{36}$ in monolayer, bilayer, and trilayer arrangements were used as model systems to simulate *ABA* bulk graphite. Structures, binding energies, and vibrational frequencies of water clusters on mono- and bilayer graphite models have been calculated, and structural changes and frequency shifts due to the water cluster-graphite interactions are discussed. ONIOM(B3LYP:DFTB-D) with coronene and water in the high level and $C_{96}H_{24}$ in the low level mimics the effect of extended graphite π-conjugation on the water-graphite interaction very reasonably, and suggests that water clusters only weakly interact with graphite surfaces, as suggested by the fact that water is an excellent graphite lubricant. A three-stage strategy is devised for *a priori* investigations of high-temperature corrosion processes of graphite surfaces due to interaction with water molecules and fragments. We predict rate constants of the reactions for water dissociative adsorption on graphite with $k_1 = 1.5 \times 10^{-27} \times \exp(-46300/T)$ cm^3/s, and $k_2 = 1.7 \times 10^{-28} \times \exp(-51100/T)$ cm^3/s for the two lowest energy pathways based on the potential surface energies of the dissociative reactions of H_2O on graphite shown in **Figure** 2.Quantum chemical molecular dynamics (QM/MD) simulations of water clusters and water addition products on the $C_{96}H_{24}$ graphite model are presented using the DFTB-D method.
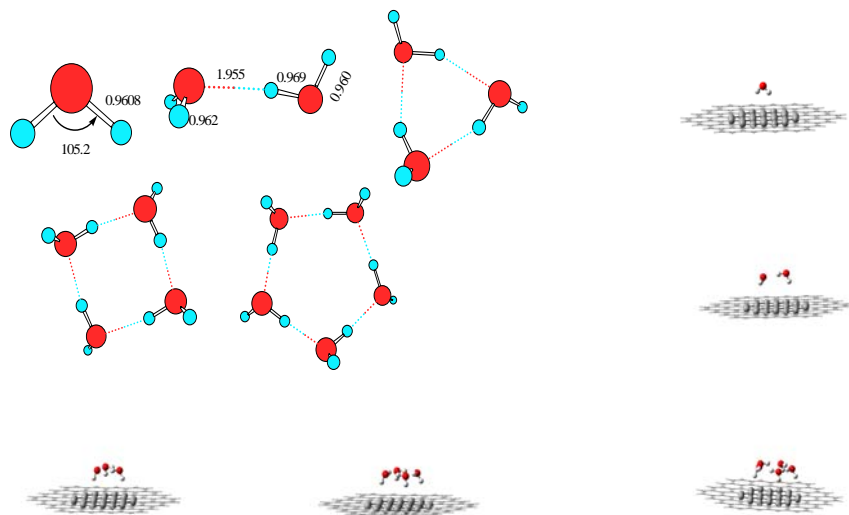
Acknowledgments

Figure 1. The optimized structures of free water clusters $(H_2O)_{n=1-5}$ and water clusters on the surface of graphite.
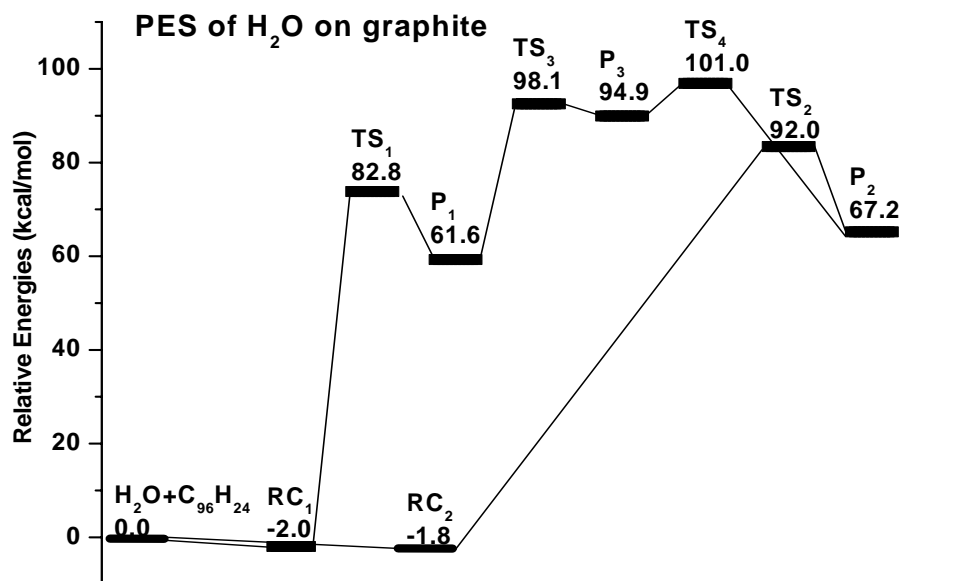

Figure 2. The potential surface energies of the dissociative reactions of H_2O on graphite.

E4. Time and Position Resolved X-Ray Scattering: An Ideal Technique to Monitor *In Situ* the Kinetics of Particle Self Assembly

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Generation of detailed mechanisms for the formation of carbon nanotubes and the gas-to-particle transition for nano-sized carbonaceous particles (soot) represent outstanding challenges for the kinetics community. Small-angle x-ray scattering (SAXS) is an ideal technique for monitoring *in situ* the nucleation and growth of nano-sized particles.[1] Third generation synchrotron x-ray sources are bright enough to allow many measurements at different positions[2] as well as time-resolved studies of induced morphological changes. We have made several advances in SAXS that allow us to perform *in situ* kinetic measurements. These include (1) an absolute calibration procedure, which allows us to compare scattering results directly to simulations, (2) extension of the technique to high values of transferred momentum, which allows us to monitor the kinetics of molecules such as benzene, and (3) the development of a detector that is capable of performing continuous measurements with a time resolution of 3.68 microsecond and pump-probe measurements with nanosecond resolution, which will allow us to perform many new and unique experiments. We will briefly review these advances and compare and contrast SAXS to *in situ* measurements performed with optical techniques. We illustrate the power of the SAXS technique with measurements of the particle mass distribution functions of incipient soot (1-2 nm), primary particles (4-15 nm), and their aggregates in a premixed flame of 15.7% ethylene, 19.2% oxygen, and 65.1% argon and compare these measurements to kinetic simulations.

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E5. In-Flight Characterization of the Heterogeneous Kinetics on NanoParticles and Nanotubes: Application of Single Particle Mass Spectrometry and Ion Mobility Measurements

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In this paper we describe two approaches for on-the-fly characterization of the reactivity of nanoparticle and nanofibers.

The first example illustrates the use of single particle mass spectrometry. Aluminum nanoparticles are being considered as a possible fuel in advanced energetic materials application. Of considerable interest therefore is a knowledge of just how reactive these materials are, and what the effect of size on reactivity is. In this paper we describe results of size resolved oxidation rate using a recently developed quantitative single particle mass spectrometer (QSPMS). Aluminum nanoparticles used were either generated by DC Arc discharge or laser ablation, or by use of commercial aluminum nanopowders. These particles were oxidized in an aerosol flow reactor in air for specified at various temperatures (25 ^{o}C ~ 1100 ^{o}C), and subsequently sampled by the QSPMS. The mass spectra obtained were used to quantitatively determine the elemental composition of individual particles and their size. We found that the reactivity of aluminum nanoparticles is enhanced with decreasing primary particle size. The absolute rates observed were found to be consistent with an oxide diffusion controlled rate limiting step. We also determine the size-dependent diffusion-limited rate constants and Arrehenius parameters (activation energy and pre-exponential factor). We found that as particle size decreases, the rate constant increases and the activation energy decreases. This work provides a quantification of the known pyrophoric nature of fine metal particles.
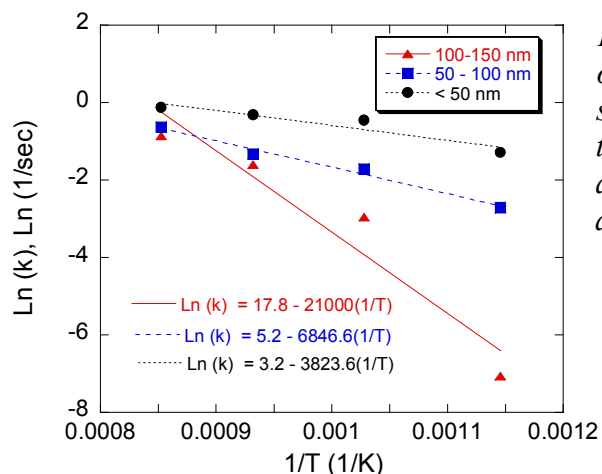

Figure 1. *Arrehenius plots (Ln (k) versus 1/T) obtained from the average rate constants (a) and size–resolved rate constants (b) at each temperature for Al particles produced from DC arc method; k is the diffusion-limited rate constant and T is the temperature (K).*

For the second example we employ mobility separation to study size changes during growth. In this paper we describe tandem mobility characterization of soot and nanofibers. We first show that we can use the electrical mobility method to characterize the surface area of aggregate particles and the length of nanofibers in free flight. We use a tandem mobility methods to study the oxidation and growth of carbon nanopartiles in the presence and absence of metals. We finds that the presence of metals in flame generated carbon particles is quantifiably different than Diesel carbon particles. However upon addition of metal to the flame generated carbon, the activation energy drops from ~160 kJ/mol to ~110 kJ/mol and is consistent with diesel particles. This later information suggests that the formation of soot in Diesel engines is catalyzed by metals. We also use the method to study the kinetics of carbon surface growth on soot particles using various organic precursors in an attempt to change the specific surface area. Finally we present results on an on-the-fly characterization of the kinetics of Carbon nanotube growth and show that gas phase growth is considerably faster than substrate grown nanotubes. We found an activation energy for growth ~ 80 kJ mol^{-1} from both acetylene and ethylene, which is considerably lower than previous works for substrate grown CNT's (E_a=110~150 kJ mol^{-1}).
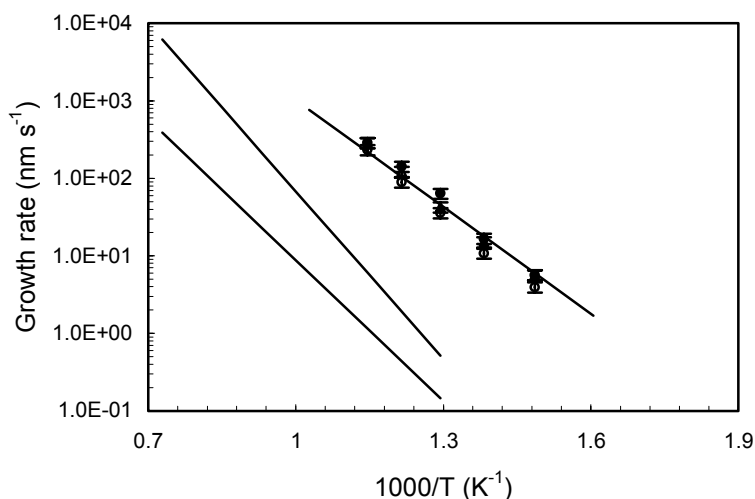

Figure 2. *A comparison of the current work with selected prior studies on the growth rate of CNTs as a function of temperature ((a) Ducati et al., E_a=117 kJ mol^{-1}; Baker et al. [5], E_a=138 kJ mol^{-1}; (c) current approach, E_a=77±2 kJ mol^{-1})*

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